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I, the below-named Chartered Patent Attorney of Tokyo Japan having an office at an address stated below, hereby declare that :

I am knowledgeable in the English and Japanese languages, and I believe that the attached English translation of the Japanese Patent Application No. 2002-326028 filed on November 8, 2002 is a true and complete translation of said application.

I also hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true ; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

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[Kind of Document] SPECIFICATION

[Title of the present Invention]

ELECTROLYTIC CAPACITOR

[Claims]

[Claim 1]

An electrolytic capacitor housing in an outer case a capacitor element formed by winding an anode electrode foil, a cathode electrode foil and a separator and by impregnating them with an electrolyte solution, wherein an electrolytic solution containing an aluminum tetrafluoride salt is used as the electrolyte solution, and wherein an electrode foil subjected to phosphate treatment is used as the anode and cathode electrode foils.

[Detailed Description of the Invention]

[0001]

[Industrial Application]

The present invention relates to an electrolytic capacitor, especially the electrolytic capacitor having a low impedance characteristic and a high withstand voltage characteristic.

[0002]

[Description of the Prior Art]

An electrolytic capacitor typically has an anode electrode foil made

of a band-shaped high purity aluminum foil where the effective aluminum foil surface has been enlarged through etching process chemically or electrochemically, and an oxide film is formed on the surface, through a chemical process of treating the aluminum foil with a chemical solution such as ammonium borate aqueous solution and the like. A cathode electrode foil is also made of an etched aluminum foil of high purity. Capacitor element is formed by the anode electrode foil and the cathode electrode foil, wound together with intervening separator made of manila paper and the like. Next, the capacitor element, after impregnating with an electrolyte solution for driving the electrolytic capacitors, is housed into a bottomed outer case made of aluminum and the like. The outer case is equipped at the opening with a sealing member made of an elastic rubber, and is sealed by drawing.

[0003]

Herewith, as electrolyte solution for driving the electrolytic capacitor having high conductivity, and to be impregnated to the capacitor element, wherein γ-butyrolactone is employed as the main solvent composed of quaternized cyclic amidin compounds (imidazolinium cation and imidazolium cation) as the cationic component and acid conjugated bases as the anionic component are dissolved therein as the solute (refer to the patent documents 1 and patent documents 2).

[0004]

[Patent documents 1] JP-H08-321440-A

[Patent documents 2] JP-H08-321441-A

[0005]

[Problem(s) to be Solved by the Invention]

However, due to the remarkable development of digital information devices in recent years, the high-speed driving frequency of micro-processor which is a heart of these electronic information devices is in progress. Accompanied by the increase in the power consumption of electronic components in the peripheral circuits, the ripple current is increased abnormally, and there is a strong demand for the electrolytic capacitors used in these circuits to have a low impedance characteristic.

[0006]

Moreover, in the field of vehicles, with the recent tendency toward improved automobile functions, a low impedance characteristic is in high demand. By the way, the driving voltage of the vehicle circuit of 14V has been progressed to 42V accompanied by the increase in the power consumption. To comply with such a driving voltage, the electrolytic capacitor requires the withstand voltage characteristic of 28V and 84V and more. Furthermore, in this field, there is a demand of using high temperature, an electrolytic capacitor, high temperature life characteristic is required.

[0007]

However, in the aforementioned electrolytic capacitor, it could not respond to such a low impedance characteristic, and its limit withstand voltage was 30V. The electrolytic capacitor was able to respond to 28V but could not reply to the demand of high withstand voltage, such as 84V and more.

[0008]

The present invention aims to supply an electrolytic capacitor having an excellent high temperature characteristic, a low impedance characteristic, and a high withstand voltage characteristic of 100V class.

[0009]

[Means for Solving the Problem]

The present invention is characterized in that an electrolytic capacitor housing in an outer case a capacitor element formed by winding an anode electrode foil, a cathode electrode foil and a separator and by impregnating them with an electrolyte solution, wherein an electrolytic solution containing an aluminum tetrafluoride salt is used as the electrolyte solution, and wherein an electrode foil subjected to phosphate treatment is used as the anode and cathode electrode foils.

[0010]

[Embodiment of the Invention]

The electrolyte solution for electrolytic capacitor of the present invention contains an aluminum tetrafluoride salt.

[0011]

As the aluminum tetrafluoride salt constituting the aluminum tetrafluoride as anion component, examples of this salt include an ammonium salt, an amine salt, a quaternary ammonium salt, or a quaternary cyclic amidinium ion as cation component, can be used. Examples of an amine constituting the amine salt include a primary amine (such as methylamine, ethylamine, propylamine, butylamine, ethylenediamine, monoethanolamine, and the like); secondary amine (such as dimethylamine, diethylamine, dipropylamine, ethy-methylamine, diphenylamine, diethanolamine and the like); and tertiary amine (such as trimethylamine, triethylamine, tributylamine, 1,8-diazabicyclo[5,4,0] undecen-7, triethanolamine, and the like). Examples of a quaternary ammonium constituting the quaternary ammonium salt include a tetraalkylammonium (such as tetramethylammonium, tetraethylammonium, tetrapropylammonium, tetrabutylammonium, methyltriethylammonium, di-methyldiethylammonium and the like) and a pyridinium (such as 1-methylpyridinium, 1-ethylpyridinium, 1,3-diethylpyridinium and the like).

[0012]

Furthermore, as for salt containing the quaternized cyclic

amidinium ion as a cationic component, the quaternized cyclic amidinium ion is a cation formed by quaternized a cyclic compound having an N,N,N'-substituted amidine group, and the following compounds are exemplified as the cyclic compound having an N,N,N'-substituted amidine group. They are an imidazole monocyclic compound (for example, an imidazole homologue, such as 1-methylimidazole, 1-phenylimidazole, 1,2-dimethyl-imidazole, 1-ethyl-2-methylimidazole, 2-ethyl-1-methylimidazole, 1,2-diethylimidazole, 1,2,4-trimethylimidazole and the like, an oxyalkyl derivative, such as 1-methyl-2-oxymethylimidazole, 1-methyl-2-oxyethyl-imidazole, and the like, a nitro derivative such as 1-methyl-4(5)-nitroimidazole, and the like, and an amino derivative such as 1,2-dimethyl-5(4)-aminoimidazole, and the like), a benzoimidazole compound (such as 1-methylbenzoimidazole, 1-methyl-2-benzylbenzoimidazole, 1-methyl-5(6)-nitrobenzo-imidazole and the like), a compound having a 2-imidazoline ring (such as 1-methylimidazoline, 1,2-dimethylimidazoline, 1,2,4-trimethylimidazoline, 1-methyl-2-phenylimidazoline, 1-ethyl-2-methylimidazoline, 1,4-dimethyl-2-ethyl-imidazoline, 1-methyl-2-ethoxymethylimidazoline, and the like), a compound having a tetrahydropyrimidine ring (such as 1-methyl-1,4,5,6-tetrahydropyrimidine, 1,2-dimethyl-1,4,5,6-tetrahydropyrimidine, 1,5-diazabicyclo[4,3,0]-nonene-5, and the like), and the like.

[0013]

As a solvent of the electrolyte solution for electrolytic capacitor utilized in the present invention, a polar protic solvent, an aprotic polar solvent, and their mixture thereof can be used. Examples of the polar protic solvent include monohydric alcohols (such as ethanol, propanol, butanol, pentanol, hexanol, cyclo-butanol, cyclo-pentanol, cyclo-hexanol, benzyl alcohol, and the like); and polyhydric alcohol and oxy alcohol compounds (such as ethylene glycol, propylene glycol, glycerine, methyl cellosolve, ethyle cellosolve, methoxy propylene glycol, dimethoxy propanol, and the like). Moreover, representative examples of the aprotic polar solvent include amide series (such as N-methylformamide, N,N-dimethylformamide, N-ethylformamide, N,N-diethylformamide, N-methyl acetamide, N,N-dimethyl acetamide, N-ethyl acetamide, N,N-diethyl acetamide, hexamethylphosphoric amide, and the like); lactone compounds (such as γ-butyrolactone,δ-valerolactone, γ-valerolactone, and the like); sulfolane series (such as sulfolane, 3-methyl sulfolane, 2,4-dimethyl sulfolane, and the like); cyclic amide series (such as N-methyl-2-pyrrolidone, and the like); carbonate compounds (such as ethylene carbonate, propylene carbonate, isobutylene carbonate, and the like); nitrile compound (such as acetonitrile, and the like); sulfoxide series (such as dimethyl sulfoxide, and the like); 2-imidazolidinone series [for example, 1,3-dialkyl-2-imidazoridinone (such as 1,3-dimethyl-2-imidazoridinone, 1,3-diethyl-2-imidazoridinone, 1,3-di(n-propyl)-2-imidazoridinone, and the like); and 1,3,4-trialkyl-2-imidazoridinone (such as

1,3,4-trimethyl-2-imidazoridinone, and the like)], and the like. Among these, γ-butyrolactone is preferably used since an impedance characteristic will improve, sulfolane, 3-methyl sulfolane, and 2,4-dimethyl sulfolane are preferably used because of their excellent high temperature characteristics, and ethylene glycol is preferably used since withstand voltage characteristic will improve.

[0014]

Further, the electrode foil subjected to phosphate treatment is used as the electrode foils. The present invention is still effective by using the electrode foil subjected to phosphate treatment as one of the cathode anode foil and the cathode electrode foil. Deterioration of both foils is prevented if this is applied to both foils so normally both foils are subjected to phosphate treatment. Normally, the aluminum foil of high purity is subjected to chemical or electrochemical etching to obtain the etching foil, however, as the electrode foil of the present invention, the etching foil obtained by performing the phosphate aqueous solution impregnation process before, during, or after the etching process is used as the cathode electrode foil. Further, as the anode electrode foil, the etching foil, the etching foil untreated with phosphate is subjected to phosphate synthesis, or the electrode foil that performed the phosphate impregnation process before, during, or after the chemical treatment is used.

[0015]

Furthermore, the effect of the present invention improves by adding the phosphorous compounds to the electrolyte solution for the electrolytic capacitor described above. Examples of phosphorus compounds and salts thereof include orthophosphoric acid, phosphonous acid, hypophosphorus acid and their salts. As the salts of the phosphorus compounds, an ammonium salt, an aluminum salt, a sodium salt, a calcium salt, and a potassium salt can be used. Moreover, examples of phosphorous compound include ethyl phosphate, diethyl phosphate, butyl phosphate, dibutyl phosphate and the like; and phosphonate such as 1-hydroxyethylidene-1,1-diphosphonic acid, aminotrimethylene phosphonic acid, phenyl phosphonic acid, and the like. Moreover, examples of phosphinate compound include methyl phosphinate, butyl phosphinate, and the like.

[0016]

Furthermore, examples of condensed phosphates include straight-chain condensed phosphates such as pyrophosphoric acid, tripolyphosphoric acid, tetrapolyphosphoric acid, and the like; cyclic condensed phosphates such as metaphosphate, hexametaphosphate, and the like, or the combination of the chain condensed phosphate and cyclic condensed phosphate. Further, as salts of these condensates, an ammonium salt, an aluminum salt, a sodium salt, a calcium salt, a potassium salt, and the like can be used.

[0017]

The addition amount is ranging from 0.05 to 3% by weight, and preferably is ranging from 0.1 to 2% by weight.

[0018]

The electrolytic capacitor of the present invention described above has a low impedance characteristic and a high withstand voltage of 100V class, and an excellent high temperature life characteristic. In other words, in case of performing the high temperature life test by using the aluminum tetrafluoride salt, the reactivity of the electrolyte solution with the electrode foil gets large due to the moisture inside the electrolyte solution, and the characteristics are affected. However, since the electrolytic capacitor of the present invention utilizes the electrode foil subjected to phosphate treatment, the reaction of the electrode foil with the electrolyte solution is controlled, whereby the high temperature life characteristic is stabilized.

[0019]

[Embodiments]

Subsequently, the present invention will be explained by using the embodiments. A capacitor element is formed by winding an anode electrode foil and a cathode electrode foil via a separator. The anode electrode foil and the cathode electrode foil are connected respectively to a lead wire for leading the anode electrode and another lead wire for leading the cathode electrode.

[0020]

These lead wires are composed of connecting members being in contact with the electrode foils, and the rod members having been molded integrally with the connecting members, and outer connecting members having been fixed at the tip of the rod members. The connecting member and the rod member are made from aluminum of 99% purity while the outer connecting member is made of a copper-plated steel wire (hereinafter CP wire). On the surfaces of the rod members of the lead wires at least, anode oxide films made of aluminum oxide are formed by a chemical treatment with ammonium phosphate aqueous solution. These lead wires are connected respectively to the electrode foils at the connecting members by means of stitching, ultrasonic welding, and the like.

[0021]

The anode electrode foil is made of an aluminum foil of 99.9% purity in an acidic solution thereby enlarging the surface area thereof through the chemical or electrochemical etching process, and then subjecting the aluminum foil to a chemical treatment in an ammonium adipate aqueous solution, to thereby form an anode oxide film on the surface thereof.

[0022]

The capacitor element, which impregnates the electrolyte solution,

is then housed into a bottomed outer case made of aluminum. The outer case is provided at the opening with a sealing member and then sealed by drawing. The sealing member has perforation holes through which the lead wires are to be passed.

[0023]

The following electrode foil was used here. The etching foil subjected to phosphate impregnation treatment in the etching process is used as the cathode electrode foil. The chemical foil subjected to anode electrode chemical film by phosphate synthesis the above etching foil is used as the anode electrode foil. As comparative example, the electrode foil that performed such phosphate impregnation treatment and phosphate synthesis was used.

[0024]

Furthermore, the used electrolyte solution for electrolytic capacitor is shown in Table 1.

[0025]

According to the electrolytic capacitors which were constructed by using the electrolyte solution of above embodiments, the rated values of the electrolytic capacitors were 100WV-22μF, and the characteristics of the electrolytic capacitor were evaluated. The test conditions are 125°C and 500 hours in the loaded state. The results are shown in Table 2.

[0026]

[Table 1]

	GBL	A	B	C	Sparking voltage (V)	Specific resistance (Ωcm)
Embodiment	79.8	20	—	0.2	205	40
Conventional example	80	—	20	—	85	91

GBL : γ-butyrolactone,

A : Tetraaluminate 1-ethyl-2,3-dimethyl-imidazolinium

B : Phthalic acid hydrogen 1-ethyl-2,3-dimethyl-imidazolinium

C : Dibutyl phosphate

[0027]

[Table 2]

	Electrode foil	Initial Characteristic		125℃ – 500 hours	
		Cap (μF)	tanδ	ΔCap (%)	tanδ
Embodiment	With phosphate treatment	23.1	0.01	−1.3	0.01
Comparative example	Without phosphate treatment	22.8	0.01	−4.3	0.03

Cap: electrostatic capacity

tanδ: tangent of dielectric loss

ΔCap: change in electrostatic capacity

[0028]

As (Table 1) clearly shows, the sparking voltage of the electrolyte solution for the electrolytic capacitor of the embodiment is high, and the specific resistance ratio is low, compared with that of the conventional example. Also, as can be seen from (Table 2), the dielectric loss of coefficient (tan δ) of the electrolytic capacitor of 100WV using this is low, the change in electrostatic capacity is low compared with that of the comparative example, tan δ is one third of the total and its effect of the present invention is clear.

[0029]

[Effect of the Invention]

According to the present invention, since the electrode foil subjected to the aluminum tetrafluoride salt and phosphate treatment is used, such that the electrolytic capacitor having a low impedance characteristic and high withstand voltage characteristic, and excellent high temperature life characteristic and leakage characteristic are provided.